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Holographic time-of-flight measurements of the hole-drift mobility in a photorefractive polymer

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The holographic time-of-flight (HTOF) technique is applied in a photorefractive polymer. The electric-field, temperature, and drift-length dependencies of the hole-drift mobility are shown to be consistent with previously published data. It is suggested that the shape of the HTOF signal reflects the degree of charge-transport disorder in this class of amorphous materials.

Photorefractivity in polymers is a rapidly expanding field. Since the first observation of the photorefractive effect in a polymer,¹ considerable progress has been achieved in the performance of these materials.²⁻⁸ The photorefractive effect originates from the space-charge field created after the redistribution of photogenerated carriers under nonuniform illumination. This space-charge field changes the index of refraction via the electro-optic effect and in this way volume holograms are recorded in photorefractive materials.⁹ It is clear that the mechanism of photorefractivity in this class of materials is remarkably different from that in inorganic crystals, with respect to the processes of charge generation, transport, and trapping and to the nonlinear optical response.²⁻⁵

Investigation with the conventional time-of-flight (TOF) technique has shown that charge transport in polymers exhibits anomalously broad TOF signals and that it is characterized by an electric-field and temperature-dependent mobility.¹⁰ The existence of photorefractivity in polymers, which is the only class of amorphous materials that exhibits the photorefractive effect, provides the unique opportunity to investigate the charge transport and trapping processes with purely optical techniques. Steady-state and transient holographic experiments, for example, have been extensively used in the case of inorganic photorefractive crystals to give valuable insight into the dynamics of the space-charge field formation and to measure the drift mobility.^{9,11-13}

In a holographic time-of-flight (HTOF) experiment, an interference pattern from two picosecond or nanosecond laser pulses creates a sinusoidal distribution of mobile carriers, which drifts under the influence of an external electric field. As charge separation advances, a space-charge field builds up that can be probed with a cw laser beam through the electro-optic effect. One measures the diffraction efficiency $\eta(t)$ (Ref. 12),

$$\eta(t) \propto (r_{\text{eff}} E_{\text{sc}}(t))^2, \quad (1)$$

where r_{eff} is the effective electro-optic coefficient and $E_{\text{sc}}(t)$ is the space-charge field. The space-charge field reaches a maximum when the mobile carriers have drifted to a position of anticoincidence with the immobile distribution of the countercharges. Further drift causes a decrease of the space-charge field until coincidence is reached again and so on. The diffraction efficiency versus time shows oscillatory behavior and from the time t_{max} that corresponds to the first maximum the drift mobility μ_{dr} can be extracted,¹²

$$\mu_{\text{dr}} = L_{\text{dr}} / (E t_{\text{max}}), \quad (2)$$

where L_{dr} is the drift length, equal to $\Lambda/2\cos(\alpha)$, where Λ is the grating spacing and α is the angle between the grating wave vector and the external electric field E . In the case where the mean-free path of the mobile charges is smaller than L_{dr} , the diffraction efficiency reaches a steady-state value monotonically.

One advantage of the HTOF technique over the conventional time-of-flight technique is that the mobility can be easily measured for different values of the drift length on the same sample. This is particularly useful in the case of polymers, as in some cases a length-dependent mobility, which is not a material parameter, can be measured due to dispersive transport.¹⁴ Furthermore, the mobility is measured in the same sample that will be used for other photorefractive measurements. Finally, the HTOF technique does not suffer from the restrictions concerning the sample thickness and the absorption length of the light used for charge generation.

The application of HTOF experiments in photorefractive polymers seems very interesting: although the physical picture of the space-charge field formation is similar with that in inorganic crystals, the nature of charge transport in disordered materials is very distinct. For this reason, it is not clear if any feature that allows the determination of mobility will be observed in the temporal behavior of the diffraction efficiency. In this paper we apply the HTOF technique in a photorefractive polymer. Contrary to the case of inorganic crystals, the HTOF signal does not show an oscillatory behavior. Despite the difference, it is shown that the HTOF technique can be successfully used to study charge transport in polymeric materials.

HTOF experiments were carried out in the photorefractive polymer composite poly(*N*-vinyl carbazole) (PVK), 2,4,7-trinitro-9-fluorenone (TNF), and 4-(hexyloxy)nitrobenzene (HONB). PVK is a well-known hole-transporting polymer, which can be sensitized with the addition of small amounts of TNF to show photoconductivity in the visible. HONB was used to provide the electro-optic functionality. The concentrations of the dopants were 0.1 wt % TNF and 40 wt % HONB relative to PVK.

HONB was prepared by a substitution reaction between 4-nitrophenol and 6-bromohexane and recrystallized from a mixture of dichloromethane and pentane (1:4). PVK was purchased from Aldrich and was precipitated three times from chloroform in diethylether. For the preparation of

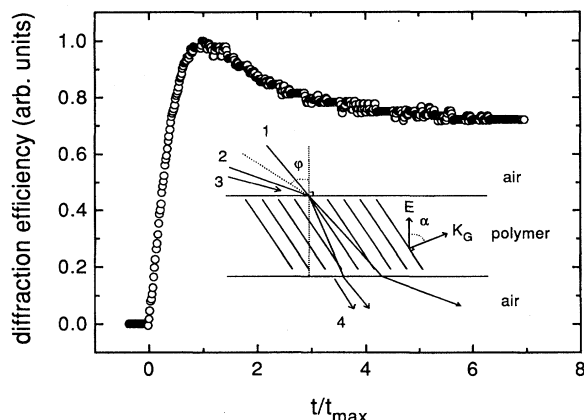


FIG. 1. Typical HTOF signal for the PVK:TNF:HONB composite at room temperature. $t_{\max}=2.7$ msec, $E=55$ V/ μm , and $L_{\text{dr}}=1.7$ μm . Inset: The experimental geometry. 1 and 2 are the writing beams; 3 and 4 are the probe and the diffracted beams, respectively.

samples, proper amounts of the three compounds were dissolved in spectroscopic grade chloroform. The solvent was extracted with a rotary film evaporator and the solid deposit was reduced into powder from which thick pellets were pressed. Subsequently, the pellets were sandwiched between two indium tin oxide (ITO) covered glass plates by heating above the glass transition temperature. Teflon spacers were used to fix the film thickness at 100 μm .

Two beam-coupling experiments¹⁵ at 633 nm have shown that the PVK:TNF:HONB composite is purely photorefractive, giving rise to asymmetric energy exchange with a gain coefficient of 3 cm^{-1} at 70 V/ μm . To the best of our resolution, no other gratings of nonphotorefractive origin were observed. The onset of absorption of HONB is below 500 nm.

For the HTOF experiments, gratings were written using two *s*-polarized, mutually coherent beams with energy fluxes 5 mJ/cm^2 [the frequency-doubled output of a single-frequency 10 nsec Nd:YAG (yttrium aluminum garnet) laser], overlapping in the sample at an external angle of 30°. The sample was tilted at an angle ϕ from the bisector of the writing beams to allow a component of the grating vector parallel to the external electric field (inset of Fig. 1). The evolution of the photorefractive grating after a single shot from the Nd:YAG laser was probed by measuring the diffraction efficiency with a Bragg-matched *p*-polarized He-Ne laser beam. As is known,² the diffraction efficiency and the readout erase time strongly depend on external electric field, tilt angle, temperature, and reading beam intensity. Thus, the He-Ne intensity was varied between 150 and 1 mW/cm^2 , maintaining a reasonable signal-to-noise ratio, while keeping the erase time longer than t_{\max} . Under these experimental conditions, the absolute value of the diffraction efficiency did not exceed 5×10^{-4} . The optical density of the samples was 0.1 at 532 nm.

In Fig. 1 a typical HTOF trace is shown. After a fast initial rise, the diffraction efficiency reaches a well-defined maximum at time t_{\max} and then decreases to a plateau value. Slow erasure by the He-Ne beam follows at longer times (not

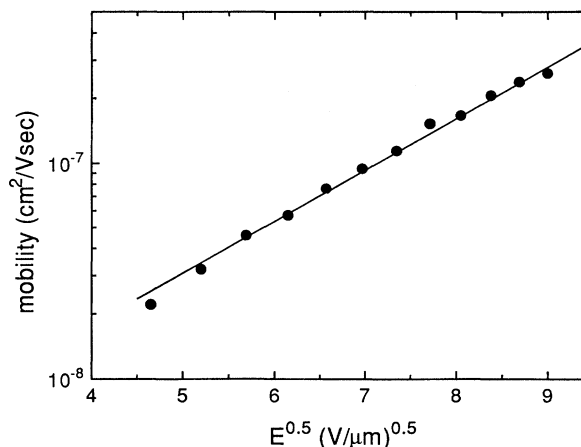


FIG. 2. The electric-field dependence of the hole-drift mobility at room temperature. The line is a fit using Eq. (3).

shown in this plot). Remarkable is the absence of any further oscillation after the maximum has been reached. A broad, dispersive decrease follows instead. Reasons for this behavior will be discussed latter.

Charge transport in PVK-based polymers is believed to be a temperature-activated hopping process.¹⁰ Gill¹⁶ has measured the electric field and temperature dependence of the drift mobility in PVK and its charge-transfer complexes with TNF and found that it can be described with the empirical equation

$$\mu_{\text{dr}} = \mu_0 \exp[-(E_0 - \beta E^{0.5})/kT_{\text{eff}}], \quad (3)$$

where μ_0 is a prefactor mobility, E_0 is the zero-field activation energy, β is a constant coefficient which represents the lowering of the activation energy due to the electric field, and T_{eff} follows the relationship

$$\frac{1}{T_{\text{eff}}} = \frac{1}{T} - \frac{1}{T_0}, \quad (4)$$

where T is the absolute temperature and T_0 is a characteristic temperature. Although the absolute magnitude of the hole mobility was found to be very sensitive to the amount of TNF, changing more than two orders of magnitude from pure PVK to pure TNF, Eq. (3) could describe all the data with a single value of the coefficient β equal to 2.7×10^{-5} $\text{eV}(\text{m/V})^{0.5}$ (Ref. 16).

In Fig. 2, the logarithm of the hole drift mobility in PVK:TNF:HONB, as calculated from Eq. (2), is plotted as a function of the square root of the external electric field. The solid line is the best fit using Eq. (3) and has a slope of 0.55 ($\mu\text{m/V})^{0.5}$, which is the same as in PVK:TNF charge-transfer complexes at room temperature.¹⁶ The fact that the same value for the lowering of the activation energy due to the electric field is measured as in PVK strongly suggests that with the HTOF technique one measures the same activated process as with the conventional TOF experiment. For β equal to 2.7×10^{-5} $\text{eV}(\text{m/V})^{0.5}$, T_0 is equal to 611 K, which is within the range from 520 to 660 K reported for the PVK:TNF composites.¹⁶

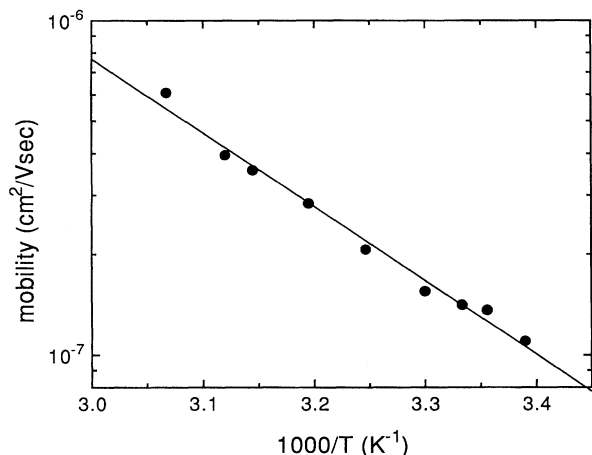


FIG. 3. The temperature dependence of the hole-drift mobility for an electric field of 55 V/ μ m. The line is a fit using Eq. (3).

The absolute magnitude of the mobility for the PVK:TNF:HONB composite corresponds to that of a composite with 0.4:1 TNF:PVK monomer unit molar ratio.¹⁶ Weiser has shown that in the latter, 61% of TNF is complexed with PVK.¹⁷ From this, it can be calculated that the actual molar ratio of nontransporting (free TNF, complexed TNF, and PVK) to hole transporting species (free PVK) is 0.85:1. In our case, this ratio is equal to the molar ratio of HONB to PVK monomer unit, which is equal to 0.35:1. This means that HONB causes a larger decrease in the hole-drift mobility compared to TNF, which is not surprising, as the presence of polar molecules like HONB is well known to decrease the drift mobility.^{18–20}

For the measurements of the hole-drift mobility as a function of temperature, the sample was put into a small oven and a thermocouple was brought into contact with it to measure the temperature. In Fig. 3 the temperature dependence of mobility is shown, together with the best fit of Eq. (3). Although the temperature range is rather limited, the mobility changes almost an order of magnitude, following the same dependence as in the PVK:TNF composites. Using a β coefficient equal to 2.7×10^{-5} eV/(m/V)^{0.5}, a zero-field activation energy E_0 equal to 0.64 eV is calculated from the slope of this line. Within the accuracy of this measurement, which is limited due to the small temperature range, this value is close to values in the range 0.65–0.68 eV reported for the PVK:TNF composites.¹⁶ The value of μ_0 in Eq. (3) can be calculated independently from the measured electric-field and temperature dependencies of the mobility. The values that were obtained are 7.8×10^{-4} and 8.2×10^{-4} cm²/(V sec), respectively, in fair agreement with each other.

By changing the tilt angle φ of the sample, the angle α between the grating wave vector and the external electric field was varied and the mobility was measured as a function of the drift length L_{dr} . As can be seen in the inset of Fig. 4, the mobility is independent of L_{dr} , in agreement with earlier measurements on PVK.²¹ This indicates that a bulk material property is measured.²²

The HTOF technique can be used to measure the mean-free path l_{free} of holes: If the drift length is made larger than the mean-free path, the well-defined maximum in the tempo-

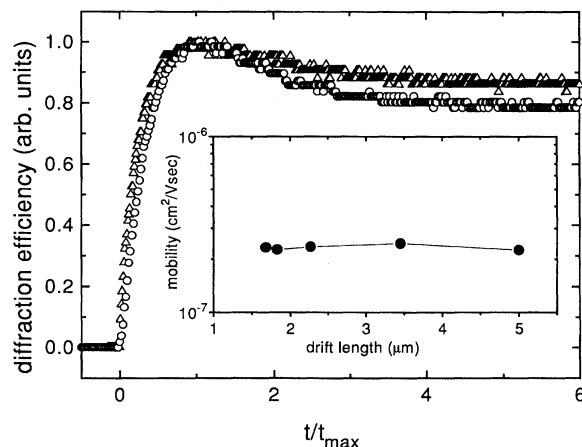


FIG. 4. HTOF traces that correspond to drift length equal to 1.7 μ m (open circles, $t_{max}=1$ msec) and 5 μ m (open triangles, $t_{max}=3$ msec), respectively. Inset: The hole-drift mobility for different values of the drift length, at room temperature and for an electric field of 75 V/ μ m. The line is a guide to the eye.

ral behavior of the diffraction efficiency will disappear. This effect was observable at low voltages, where the drift mobility is small.

As mentioned above, the HTOF signal does not show an oscillatory behavior. According to the model with a constant mobility for all the charge carriers, the diffraction efficiency grows as a function of time according to the equation¹²

$$\eta = \eta_{\infty} [1 - \exp(-\Gamma t)]^2, \quad (5)$$

with

$$\Gamma = (\tau^{-1} + K_G^2 D) - i K_G \mu_{dr} E, \quad (6)$$

where τ is the deep trap lifetime, K_G the grating wave vector, and D the diffusion coefficient. A more sophisticated model that includes shallow traps predicts essentially the same dependence.¹³ The imaginary part of Γ is responsible for the oscillation, while the real part defines the speed of grating growth and the damping of the oscillation. Using Eq. (5) it was not possible to fit the shape of the HTOF signal (Fig. 1), which indicates the inapplicability of this simple model in the case of photorefractive polymers.

One possible reason for the absence of oscillation could be that holes suffer extensive recombination when they arrive at coincidence with the distribution of the counter-charges (former bright fringe area). In this case, the shape of the transient would have strongly depended on the contrast of the interference pattern. To verify that, the intensity of one of the beams was decreased 10 times but no change was observed in the shape of the HTOF trace (except for a change in the amplitude).

The absence of oscillation is not due to a small mean-free path: in Fig. 4, the HTOF traces corresponding to L_{dr} equal to 1.7 and 5 μ m are shown, as a function of t/t_{max} . Although the width of the latter is broader, a well-defined maximum is also observed, indicating that the mean-free path of the holes at 75 kV/ μ m is larger than 5 μ m. This means that l_{free} is

sufficiently larger than the drift length for the curve that corresponds to L_{dr} equal to $1.7 \mu\text{m}$.

The shape of the HTOF signal can be explained only as a result of the energetic and positional disorder of the hopping sites. Due to the presence of such disorder, an anomalously broad distribution exists in the velocity of the mobile holes,²² which causes a smearing out of the oscillation in the HTOF signal.

In the conventional TOF measurement, the mobility is calculated from a log-log plot of the current versus time. The arrival time is taken as the point that corresponds to the crossing of the asymptotes that describe the two regions of current, which mainly monitors the arrival of the fastest holes.¹⁴ Less often, the point at which the current drops to half of its plateau value is used to calculate the mobility. The two approaches can lead to values that differ by as much as a factor of 2.²² In our case, the mobility was calculated from the time that corresponds to the maximum of the diffraction efficiency, which follows the center of charge of the hole distribution. A theoretical framework for HTOF experiments

that considers the dispersive character of charge transport in polymers is needed in order to compare absolute values of mobility with those from conventional TOF and computer simulations. This may also allow one to extract information concerning the degree of charge-transport disorder from the shape of the HTOF signal.

In conclusion, the influence of the nature of charge transport in amorphous materials on the shape of the HTOF signal is observed. The applicability of the HTOF technique in the measurement of the drift mobility in photorefractive polymers is demonstrated. The measured electric-field, temperature, and drift-length dependencies of the hole-drift mobility in the composite PVK:TNF:HONB are in agreement with literature data for PVK.

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